



The deactivation of photocatalytic based air purifiers by ambient siloxanes

Stephen O. Hay*, Timothy N. Obee, Catherine Thibaud-Erkey

United Technologies Research Center, 411 Silver Lane, East Hartford, CT 06108, United States

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ABSTRACT

One of the more promising applications of ultraviolet photocatalytic oxidation (UVPCO) technology is air purification for improved indoor air quality (IAQ). Successful implementation has been hindered by lack of understanding of the behavior of UVPCO systems in real, constantly evolving ambient air environments. The focus of most published research is on the demonstration of the rate of removal of various single compounds in a laboratory experiment, often at high concentrations relative to those encountered in ambient air. UVPCO products have been released worldwide with wildly varying claims of effectiveness and lifetime, but limited data is available relative to the long term effectiveness of this promising technology.

This study presents results from laboratory photocatalyst deactivation studies, and field testing of prototype reactors in two office building locations in CT, USA. The goal was both to investigate deactivation by silicon-containing volatile and semi-volatile organic compounds (VOCs and SVOCs) and to determine the durability of the photocatalyst *in situ* in an office environment. Ambient air quality was monitored by total VOC sensors, and relative humidity and temperature were documented. Limited air analysis was performed. Photocatalysts employed in the testing were either Degussa P25 or a 3% WO₃ coated P25. The results indicate that rapid catalyst deactivation is observed in photocatalytic air purifiers deployed in ambient office air.

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1. Introduction

Deactivation of metal-based thermal catalysts through coking and poisoning is a very well documented phenomenon [1]. However, deactivation of photocatalysts has only recently attracted attention, possibly because these catalysts have only recently been commercialized. A 1996 literature survey on photocatalytic air treatment and purification by Sauer and Ollis [2] highlighted the occurrence of photocatalyst deactivation in previous studies and the need for additional research on the topic to support commercialization of photocatalysis systems. Thereafter, various authors specifically studied the deactivation of photocatalysts (in particular TiO₂) during the oxidation of various species such as toluene [3], nitrogen-containing compounds [4,5] ethanol [6] and octamethyltrisiloxane [7]. In all cases, deactivation was noted, sometimes accompanied by yellow discoloration of the catalyst [3,8].

Thermal and photocatalytic regeneration were evaluated and were found to allow partial to complete recovery of initial oxidation rates. In particular, our group studied the thermal regeneration of TiO₂ deactivated during toluene oxidation and found that a temperature of 420 °C was required to achieve complete regeneration in air. Jacoby et al. [8] studied benzene photocatalyzed

oxidation and catalyst regeneration using flowing air and UV light and showed that the catalyst could be regenerated by a 20 h treatment that also restored the catalyst to its original white color. Following photocatalytic deactivation during octamethyltrisiloxane oxidation, chemical treatment of the catalyst with a dilute alkaline solution was successfully used by Sun et al. [7] partially reactivate the catalyst.

Sun et al. [7] also proposed a scheme for the deactivation mechanism of TiO₂ thin films due to siloxane groups, suggesting the formation of silanol (Si-OH) groups on the surface leading over time to the deposition of a layer of SiO_x on the catalyst thereby deactivating the catalyst. Lewandowski and Ollis [9] proposed a two-site kinetic model for deactivation due to aromatics. This model was shown to adequately represent their experimental data.

Deployment of photocatalytic based air purifiers in ambient air represents a drastic departure from the controlled laboratory environment. There are literally hundreds of compounds present in indoor air with concentrations that vary with temperature humidity, occupancy and other environmental variables. Deactivation rates and processes by individual species and from possible synergistic interaction of distinct species make the prediction of air purifier performance based solely on laboratory data a real challenge. Consequently, to obtain performance data we have opted to deploy air purifiers in commercial buildings in France and the USA. The data indicated that catalyst deactivation dominates the performance.

* Corresponding author. Tel.: +1 860 610 7198; fax: +1 860 660 1162.

E-mail address: hayso@utrc.utc.com (S.O. Hay).

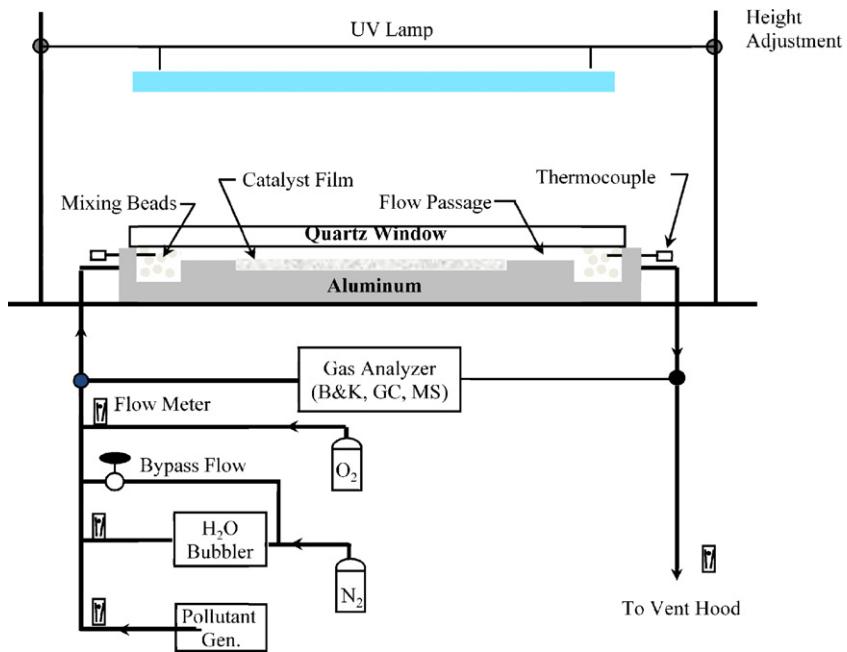


Fig. 1. A schematic diagram of the flat plate reactor used in laboratory deactivation testing.

2. Experimental

Photocatalytic laboratory studies were performed in an intrinsic rate reactor, described in detail elsewhere [10–12] and shown in Fig. 1. Catalyst activity was calculated from the experimentally measured disappearance of a propanal precursor at steady-state by referencing propanal removal efficiency to a control. The titania based photocatalyst employed were either Degussa P25, used as received from Degussa, or 3 wt% WO₃ coated on Degussa P25 whose preparation is described elsewhere [13]. Photocatalyst monoliths were prepared by dip coating or spray-coating a 20% by weight

suspension of the catalyst in deionized water. A Brüel & Kjaer 1302 photoacoustic detector was employed to monitor water concentration and propanal concentrations were measured using an Agilent 6890N GC equipped with a FID detector.

Ambient air testing was done in a prototype air purifier designated as SSVR (sub-scale validation reactor). A schematic of this reactor is shown in Fig. 2 (upper trace). This purifier was a 0.3 m × 0.3 m fiberglass duct fitted with a dust filter at one end and a fan (Fantech FX 10 XL) at the opposite end, which served to pull air through the filter into the duct exiting through the fan. The fan was connected to a Variac, allowing adjustment of the fan speed

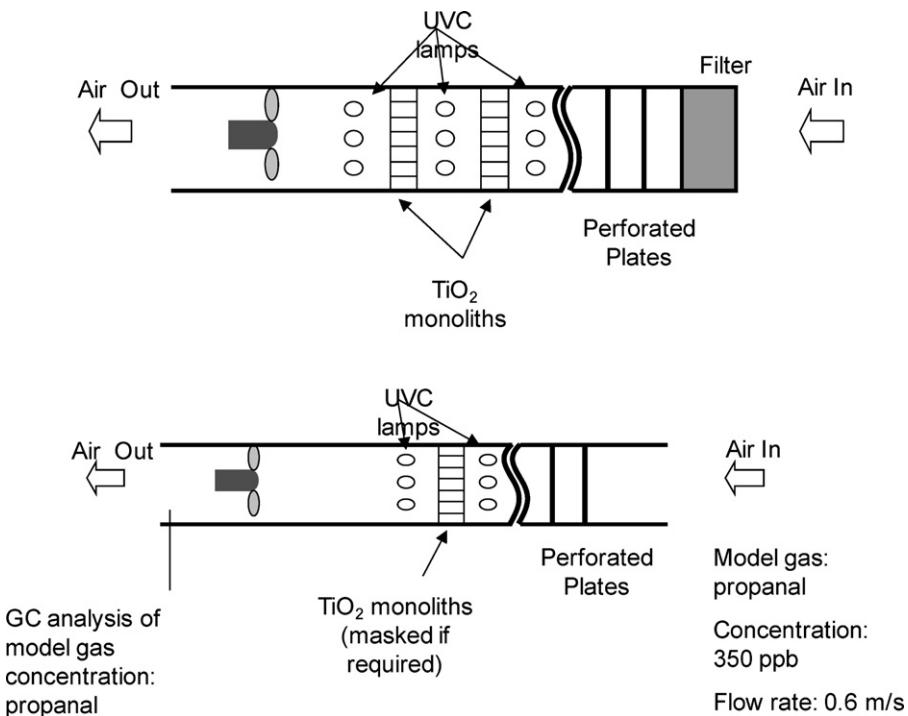


Fig. 2. Upper: A schematic diagram of the prototype air purifiers deployed in ambient air testing. Lower: A schematic diagram of the activity test facility used to determine the activity of catalyst monoliths deployed for ambient air testing.

and of the flow through the purifier. Each reactor was equipped with three rows of four UVC lamps (Philips TUV 16W T5 4P-SE) and two $0.3\text{ m} \times 0.3\text{ m} \times 0.025\text{ m}$ catalyst coated monoliths were placed between the rows of lamps. This provided reasonably uniform UVC irradiance, of about $3\text{--}4\text{ mW/cm}^2$, on each face of the monolith.

The activity of the photocatalyst monoliths was determined in a specially designed test facility in the laboratory. The test facility (shown schematically in Fig. 2, lower trace) consisted of a ca. 3.7 m long fiberglass ductwork, a fan, two banks of UVC lamps, and perforated plates. The fan, which was identical to the fan deployed with the air purifiers, was located at the exhaust end and pulled ambient laboratory air through the duct at ca. 0.6 m/s . The exhaust was vented into a laboratory hood with external exhaust. The challenge gas employed was a 100 ppm propanal standard in nitrogen (Matheson). The gas was injected at the inlet of the duct and was diluted to a uniform flow of desired concentration through a series of perforated plates that acted as flow straighteners and mixing fans (not shown). The propanal concentration after dilution was ca. 350 ppb by volume. Two rows of four UVC lamps (identical to those in the SSVR air purifiers) surrounded the space where the monolith to be tested was placed. A control monolith was always employed and was tested at identical conditions as the candidate monolith. This allowed testing to be independent of ambient humidity and helped to correct for any fluctuations in the ambient volatile organic compound (VOC) background. The control monolith was coated with photocatalyst during the same batch preparation as the catalyst monoliths being studied in the ambient air test. All activity was calculated relative to the activity of the control monolith. The percent remaining activity was calculated as the single pass efficiency (SPE_1) of the catalyst monolith from the air purifier divided by the single pass efficiency of the control monolith (SPE_C):

$$\text{Remaining activity\%} = \frac{\text{SPE}_1}{\text{SPE}_C} \times 100\% \quad (1)$$

$$\text{SPE} = \frac{[\text{propanal}]_{\text{inlet}} - [\text{propanal}]_{\text{outlet}}}{[\text{propanal}]_{\text{inlet}}} \quad (2)$$

Conversely, percent deactivation is simply 100% minus the percent remaining activity. The single pass efficiency is defined in Eq. (2) as: one minus the difference observed in the propanal concentration divided by the inlet concentration. As above, a Brüel & Kjaer 1302 photoacoustic detector was employed to monitor water concentration and propanal concentration was measured using an Agilent 6890N GC equipped with a FID detector.

The concentration of ambient siloxanes was determined by active air sampling using Tenax sampling tubes. Ambient air was drawn through the Tenax packed stainless steel tube at a predetermined flow rate for a set period, enabling the volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs) in the air to adsorb onto the Tenax sorbent. The ambient air contaminants adsorbed on the Tenax were then desorbed in a Scientific Instrument Services, Inc. Short Path Thermal Desorption Unit Model TD-4. The thermal desorption unit was connected to a Hewlett Packard 6800 Series GC which was fitted with a 5973 Mass Selective Detector. The GC/MS system was calibrated for siloxanes and other VOCs of interest.

3. Results and discussion

3.1. Analysis of field units

A full-scale photocatalytic air purifier was deployed in a technical education center at UTRC (United Technologies Research Center, East Hartford, CT) in order to validate the ability to improve indoor air quality with UVPCO-based air purification. We also wished to verify catalyst longevity. Our preliminary investigations

Table 1

A breakdown of the XPS results for 95 catalyst samples exposed to ambient air in France or Connecticut, USA. Silicon and Carbon were prevalent.

Location (duration)	Observed XPS at% ratio		
	Si/Ti	C/Ti	N/Ti
France #1 (2 months)	1.3	0.7	0.2
France #1 (18 months)	0.7	1.1	0.1
France #1 (21 months)	1.5	1.3	0.2
France #2 (13 months)	0.3	2.6	0.3
USA #1 (3 months)	1.2/-0.2	8.2	0.7
USA #2 (0.75 months)	0.9	0.1	0.1
USA #2a (0.75 months)	0.4	0.2	<0.1

indicated that catalyst longevity was significantly shorter than expected.

In an effort to understand the deactivation of photocatalytic air purifiers deployed in ambient air, we collected samples of catalyst monoliths from air purifiers that had been in service in ambient air in commercial buildings located in USA, France and Denmark for periods ranging from 2 months to 18 months and tested them for activity. The catalyst used was either a 100% Degussa P25 or a ca. 50% Degussa P25, 50% Millenium-50 that had been dip-coated on an aluminum honeycomb monolith. In all cases, we observed complete deactivation for all 95 recovered monoliths. A few of the monoliths were afterwards exposed to UVC radiation for 24-h and were found to partially reactivate.

Samples of the catalysts were taken and subjected to XPS surface analysis. The analysis revealed that sulfur, chlorine and phosphorus were below detection limits, nitrogen was detectable, and silicon and carbon were conspicuous. The results, which are shown in Table 1, are expressed as ratios of the observed atomic percent of the species of interest (silicon, carbon, or nitrogen) to the atomic percent of titania which was the dominant signal observed. The reported ratios are averages of at least two different spots on the catalyst surface. This allowed more accurate comparison between different catalyst monolith samples. In all cases, the silicon, carbon and nitrogen signals disappeared with sputtering into the surface of the catalyst sample until only the expected Ti and O was observed. No analysis of the ambient air in each location exist, so we can only infer from the XPS that silicon and carbon containing compounds were present in the ambient air during the lifetime of the prototype air purifiers and may have lead to the observed deactivation. Ambient air can contain literally hundreds of contaminant species [14]. Most of these species contain carbon but only a few silicon-containing species have been identified, the most prevalent of which belong to the family of compounds termed siloxanes. Ambient air siloxanes have been reported to cause the growth of SiO_2 crystals on electrostatic precipitators [15,16] and the growth of amorphous silica on electrical contacts [17], both operating in oxidizing environments.

An electron microprobe (EMP) analysis was performed on several samples and analysis (see Fig. 3) indicated the presence of a silicon rich layer on the outer (the side or face exposed to ambient air) portion of the photocatalyst. Shown is a fragment of a coating from a purifier that had been deployed in France. The micrograph corresponds to a titania photocatalyst coating where the top of the trace had been bonded to the aluminum honeycomb monolith and the bottom of the trace corresponds to the surface of the catalyst exposed to UVC light and ambient air for ca. 18 months and exhibiting no photocatalytic activity when removed and tested. It can be readily seen in the X-ray map inserts that a silicon rich layer on the order of $230\text{--}260\text{ nm}$ has formed. The titanium and oxygen are dispersed evenly throughout the coating as one would expect. The total observed thickness of the catalyst layer on the monolith was ca. $15\text{--}20\text{ }\mu\text{m}$ of which approximately $10\text{ }\mu\text{m}$ (depth measured

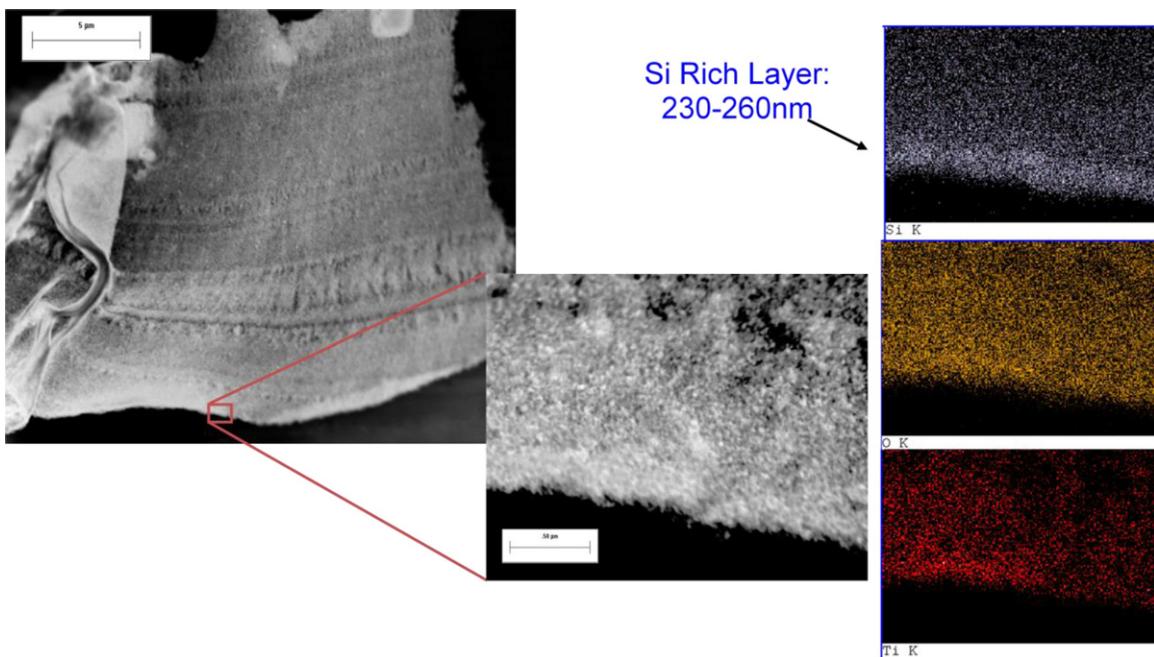


Fig. 3. Micrographic data from the electron microprobe. The left trace is the catalyst layer removed from a photocatalyst deployed in an air purifier in an office building in France. The insert highlights the portion of the catalyst surface that was exposed to ambient air. The three traces to the right shows the mapping of titanium (red,) oxygen (yellow) and silicon (silver) respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.).

from the surface exposed to the UVC radiation) is active [18,11]. If the observed silicon is due to oxidized siloxanes, one would expect to find it as silicon dioxide (silica.) The working hypothesis was that irreversible deactivation occurred on the surface of the photocatalyst due to build-up of silicon dioxide formed from photo-oxidation of siloxanes found in ambient air.

In order to further understand this phenomenon, we undertook a series of controlled laboratory experiments to determine how silicon-containing VOCs would oxidize on a photocatalyst surface and affect photocatalyst performance. In addition, analysis of ambient air for species content was carried out to establish a correlation between the laboratory tests and the deactivation observed in the real world.

3.2. Laboratory catalyst deactivation

A Degussa P25 wash-coated microscope slide was exposed to UV irradiation and ca. 1 ppmv tetramethylsilane (TMS) in an 80:20 $\text{N}_2:\text{O}_2$ carrier gas mixture for various exposure times ranging from 30 min to 24 h. Catalyst activity was measured using propanal as described above. Activity was observed to decline steadily as exposure period increased. XPS analysis was performed in the area of the slides exposed to the UV and TMS to measure the amount (atomic percent) of silica that had accumulated on the surface from photocatalytic action. The results are presented in Fig. 4 in a semilog plot that shows a strong correlation between the extent of deactivation and the silica observed on the catalyst.

A TEM analysis was performed on the near totally deactivated photocatalyst surface. The results are presented in Fig. 5. An amorphous layer assigned to SiO_2 is readily observed in both traces as are the crystallites of Degussa P25 TiO_2 . It appears that the photocatalytic action has mineralized TMS to silicon dioxide which has formed on the outer surface of the catalyst crystallite and on itself, bridging the gap between crystallites and between the P25 agglomerate particles. It is readily apparent that silica build up in the outer layer of a photocatalyst could seal the interior regions to access by gaseous species resulting in total deactivation of the catalyst monolith.

3.3. Ambient air testing

Four prototype air purifiers (SSVR) were deployed in separate locations within UTRC, a corporate training center, a lobby area, an empty office and a conference room. Catalyst monoliths were coated with a 3% by weight WO_3/TiO_2 catalyst. Each catalyst monolith was baselined for catalyst activity in our catalyst monolith test facility and retested after ca. a week of continuous operation.

Decreased activity was observed in all cases ranging from 55% to >90% deactivation after 1-week of operation. Since such significant deactivation was observed, a second series of ambient air tests were performed. The four SSVRs were refitted with fresh catalyst. Two were given catalyst monoliths coated with Degussa P25 titania and two were again deployed with the WO_3/TiO_2 catalyst. This insured against the observed phenomenon being related to use of the modified P25 catalyst. Again, significant deactivation (28–80%) was observed. XPS analysis was performed on each of the catalyst monoliths involved in both series following 1-week exposure tests. The observed atomic percent of siloxane is shown plotted against the observed percent deactivation in Fig. 6. Also shown (black squares,) are the results from the laboratory deactivation

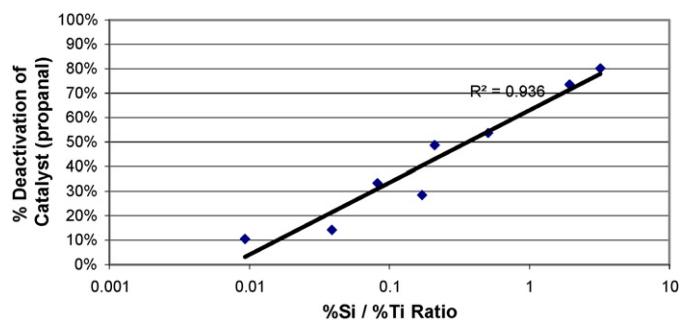


Fig. 4. The extent of deactivation, induced on a Degussa P25 wash-coated microscope slide by exposure to TMS and UVC radiation in the flat plate reactor, plotted as a function of the log of the ratio of percent silicon to percent titanium as determined by XPS analysis.

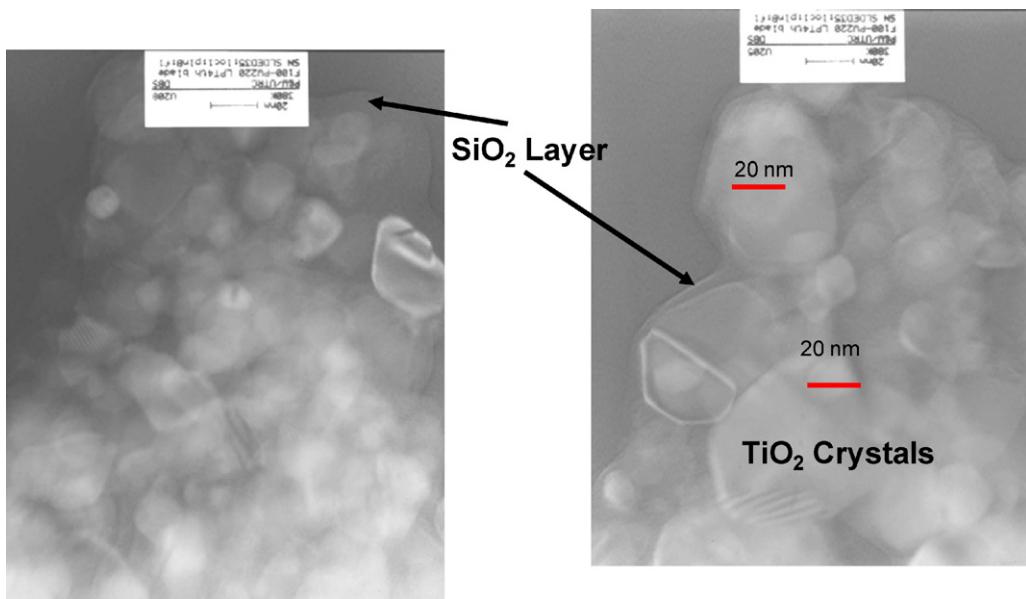


Fig. 5. A TEM of photocatalyst exposed to TMS and UVC radiation in the flat plate reactor until 80% deactivated. Amorphous silica layers are clearly visible surrounding the crystalline titania.

testing discussed above from Fig. 4. The results are not presented as a ratio relative to the atomic percent of titanium as there was significant carbon observed on the surface of the catalyst exposed to ambient air which obscured the titanium XPS signal. Collectively all the data shown in Fig. 6 points to a correlation between the observed deactivation in ambient air and the silica observed on the catalyst surface. The outlying data points are an indication that deactivation in ambient air is complex, likely involves multiple mechanisms and deserving of further study. It is worth reiterating that the ambient air environment is complex and is an ever evolving mixture of ca. hundreds of VOCs and SVOCs whose presences and concentration depend on such environmental variables as temper-

ature, humidity, occupancy, materials of construction, furnishings, etc. The XPS data indicates that a correlation exists between the silica observed on the catalyst surface that is similar to that observed when a silane-exposed photocatalyst deactivated in controlled laboratory tests. There is little or no silane in ambient air but there are generally several siloxanes present at sub ppm levels. This points to siloxane-induced deactivation as the cause of the photocatalyst deactivation observed in ambient air, but this may not be the only deactivation occurring process.

To gain further understanding of photocatalyst deactivation kinetics in real environments, the four SSVR were deployed in two separate locations. Two were located in a corporate training center, the other two in a commercial office spaces in CT. Again each air purifier contained two catalyst monoliths. As before, each catalyst monolith was baselined for catalyst activity in our catalyst monolith test facility (described above) and then retested weekly. Total hours of lamp-on time were logged and sporadic ambient air samples were taken and tested for siloxanes. CO₂ and RH (relative humidity) sensors were co-located with the air purifiers to allow us to monitor total air quality. One of the two SSVRs in each location was equipped with a proprietary activated carbon based filter designed to remove siloxanes from the ambient air, the other (denoted as *unprotected*) was not. With this exception the SSVRs were identical and deployed side by side or over/under. All reactors were deployed with Degussa P25 coated monoliths, flow rates were set at 2.8 m/min and verified weekly. Activity testing was performed weekly as discussed above.

The results varied dramatically between the paired air purifiers. Unprotected catalyst monoliths were observed to deactivate totally in ca. 1000 h of operation (see Fig. 7) while the catalyst monoliths protected by the adsorption filter retained ca. 60% activity at 1000 h of operation. In each location the unprotected catalyst suffered rapid deactivation and the time dependence of the deactivation obeyed a simple exponential decay (average data shown as a red dashed line).

Some evidence of reversible deactivation was observed during activity testing of the catalyst monoliths. Ambient air sampling of siloxanes was performed. We have the ability to quantitatively detect the five most prevalent siloxanes found in ambient air based on calibration of our GC/MS system. We found an average

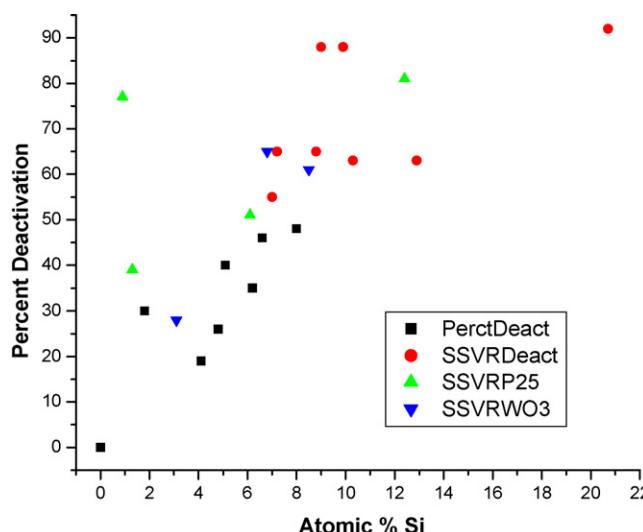


Fig. 6. A plot of percent deactivation versus atomic percent silicon (from XPS data) for the TMS deactivated laboratory slides (black squares), the first deployment of the prototype air purifiers (SSVR) in ambient air with WO₃/P25 photocatalyst (red circles), the second deployment of the SSVR with WO₃/P25 photocatalyst (blue inverted triangles), and the second deployment of the SSVR with P25 photocatalyst (green triangles.) A correlation is evident in all cases. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.).

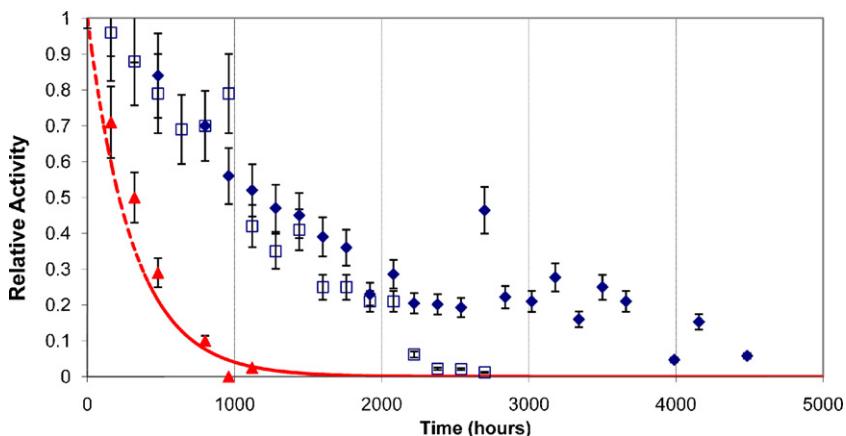


Fig. 7. A plot of activity versus hours of operation is shown for three SSVR deployed in two locations. In each location one SSVR had no filter to remove siloxanes and decayed in ca. 1000 h (red triangles). A second SSVR in each location was protected from gaseous siloxanes by an activated carbon based filter media (diamonds and open squares). This extended the observed lifetime by 2–3 times. The red dashed line represents a simple exponential fit to all deactivation tests done with an unprotected catalyst. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.).

concentration of 0.2 ppbv siloxanes with DMCPS (decamethylcyclopentasiloxane) being by far the most prevalent. Total VOC and RH sensors showed no unusual activity, just typical variations expected for an office environment.

If we look at the activity decay of the protected catalyst monoliths, we see that its lifetime has been extended by a factor of 2 or 3. This indicates that species in ambient air, which are removed by the filter, are causing the deactivation. In light of the observed correlation between silica found on the surface of the catalyst and the deactivation observed, we believe that siloxanes found in ambient air are oxidized on the surface of the photocatalyst and form an amorphous silica layer that serves to cap the surface of the porous catalyst structure resulting in deactivation.

On several occasions it was noted that the SPE (i.e., propanal activity determinations) being measured was initially time dependent. In all cases, SPE was allowed to stabilize before recording the SPE data. It is quite likely that this was an indication of reversible deactivation caused by oxidizable species that coated the photocatalyst surface. This reversible deactivation was more prevalent as the activity of the surface decreased and was rarely observed at activities over 50%. It is possible that as deactivation proceeds due to the photocatalytic action on siloxanes the catalyst surface becomes partially covered with amorphous silica. As the active surface area decreases, total hydroxyl formation decreases and the catalyst is more susceptible to chemisorption by VOCs. This type of chemisorption has been previously observed [19] to cause reversible deactivation. As the catalyst is exposed to UVC light in the activity test facility without the presence of the VOC (or VOCs) which caused the reversible deactivation, activity is restored to the limits defined by the silica coverage. It is plausible that photocatalytic based air purifiers, in reality, have shorter lifetimes than observed in our testing due to a reversible deactivation that precipitously deactivated the stressed catalyst surface once the siloxanes induced deactivation has caused significant surface blockage.

4. Conclusions

We have observed near total photocatalyst deactivation in photocatalytic technology based air purifiers deployed in office environments for ca. 1 year. Electron microprobe examination of selected catalyst monoliths discovered a silicon rich layer ca. 200 nm thick at the edge of the catalyst layer exposed to ambient air. In forced deactivation experiments conducted in the laboratory with TMS, a strong correlation was observed between the atomic percent of silicon on the surface and the extent of deactivation.

A similar correlation was observed in deactivated photocatalyst monoliths from prototype air purifiers deployed in ambient air in office locations. Since siloxanes are the prominent silicon-containing VOC or SVOC found in ambient air, this is a strong indication the deactivation in ambient air is due to the photooxidation of siloxanes. In laboratory testing it was observed that the result of photocatalytic action on TMS was an amorphous silica layer that formed on the outer surface of the catalyst layer, effectively sealing off access of gas phase molecules to the remaining photocatalyst. A similar silica layer formed by photocatalytic action on siloxanes in ambient air would explain the observed deactivation. We have also shown that the lifetime of a photocatalytic based air purifier in ambient air can be extended through the use of an adsorbent filter selected to capture large molecular weight compounds. Much more study is warranted to understand how photocatalytic based air purifiers can be deployed in ambient air without deactivation induced lifetime shortening.

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